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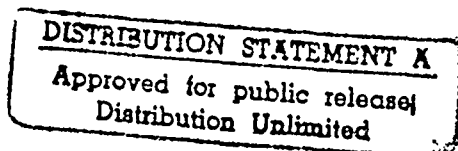
The Annual Report is hereby submitted in accordance with the requirements of contract number N00014-85-C-0421.



Respectfully yours,

A handwritten signature in cursive script that reads "John G. Smeggil".

John G. Smeggil



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Study of Adherent Oxide Scales
Contract No. N00014-85-C-0421

R89-917259-1

Reported by: J. G. Smeggil
United Technologies Research Center
East Hartford, CT

February 15, 1989



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I. INTRODUCTION

→ In the presence of ambient environments at elevated temperatures, all structural alloys are thermodynamically unstable reacting to form oxide scales. In order for such thermally grown oxide scales to be protective, they must limit the reaction rate between atmospheric oxygen and the substrate alloy. Oxidation rates are limited by scales which exhibit these properties: (1) slow growth kinetics; (2) minimal vaporization effects at temperatures of interest; (3) minimal interaction with molten salts which might be present on hardware surfaces; and (4) adherence under thermal cycling conditions.

For most alloys which form either alumina or chromia scales, the latter most property—oxide scale adherence under thermal cycling conditions—controls service life. *key words*

To achieve enhanced oxidation resistance, low levels of reactive elements such as yttrium, zirconium, etc. have frequently and repeatedly been documented in the literature to promote beneficial adherence effects. As might be expected with the positive improvements achieved from small additions of reactive elements, numerous studies have been conducted over the years to try to identify the cause of their benefit. Despite extensive studies conducted over many years, there has been no general consensus as to the mechanism responsible for the improvements observed. Several mechanisms reported in the literature to account for factors the improvements observed include the following:

- (a) the formation of oxide pegs which "anchor" the scale to the substrate (1);
- (b) the prevention of vacancy coalescence at the scale-substrate interface by providing for alternative coalescence sites (2);
- (c) increased oxide scale plasticity (3);
- (d) modification of oxide growth processes (4);
- (e) formation of graded scales which would minimize thermo-mechanical differences (5); and
- (f) modification of bonding forces through preferential segregation of the active element to the scale-metal interface (6).

While the above effects have been suggested to occur for both alumina and chromia scales, in only the case of chromia scales the formation of mixed yttria-chromia scales has additionally been suggested to account for benefits observed (1).

Previous studies conducted at UTRC have indicated that an additional, previously unappreciated effect strongly influences the adherence of alumina oxide scales (7,8). Based on this work sulfur indigenously present at low levels (approximately 20 to 40 ppm) segregates to the free metal surface at elevated temperature as primarily documented by

Auger studies (8-11). With the addition of an active element, the surface segregation of sulfur is markedly reduced (8, 11). These findings suggested that for similar experiments conducted in atmospheres and conditions which would promote the formation of an oxide scale similar segregation effects would occur.

However in the presence of a barrier oxide layer, sulfur segregation would be to the critical scale-metal interface rather than to the free metal surface in the high vacuum chamber of an Auger spectroscope. This segregation has been observed by UTRC (12) and has subsequently been confirmed by other authors (9). UTRC studies have shown based on Auger, ESCA (Electron Spectroscopy for Chemical Analysis) and EDAX (Energy Dispersive X-ray Analyses) that for the alumina former Ni-20 wt. % Cr-12 wt. % Al the sulfur present at the interface was there as a refractory sulfide as well as a moiety with properties similar to elemental sulfur (12).

Using this information as a basis, UTRC conducted experiments which have demonstrated that, by reducing the sulfur content of the alumina-forming alloy Ni-20Cr-12Al, oxide scale adherency was strikingly improved. In the case of both 1050° or 1180°C cyclic testing, standard alloys of Ni-20Cr-12Al typically containing approximately 30-40 ppm sulfur as determined by GDMS (glow discharge mass spectrometry) techniques showed poor oxide scale adherence. By reducing the sulfur content to the approximately 1-2 ppm level, oxide scale adherence was markedly improved effectively equivalent to that produced on alloy with reactive element, i.e. yttrium, additions (13).

These findings related to the adherency of protective alumina scales have been confirmed and substantiated by other experimenters (14).

While alumina formers are important for high temperature applications where simple oxidation is the primary concern, numerous applications exist at lower temperatures where concerns about hot corrosion resistance rather than oxidation predominate. To address this issue, the objective of the current work has been to determine if indigenous sulfur is similarly an important factor in the adherence of chromia films.

II. EXPERIMENTAL PROCEDURES AND MATERIALS

In selecting a typical chromia-former, the alloy Ni - 40 wt. % Cr was chosen. Alloys of conventional high purity starting elements were prepared by standard vacuum metallurgy techniques. For conventional standard purity alloys, 99.9 wt. % chromium and 99.99 wt. % purity chromium were used. Alloys from high purity, i.e. specifically low sulfur level, metals purchased from MRC were prepared by arc melting small (approximately 20 gram) buttons. All prepared ingots or buttons were homogenized in hydrogen for 24 hours at 1200°C prior to sectioning. After metallographic sectioning, specimens were ground to 600 grit SiC prior to oxidation experiments.

Typical analyses of alloy materials used here are:

<u>Ingot Designation</u>	<u>Wt.% Cr*</u>	<u>S (ppm by wt)**</u>
Normal purity	40.00 (0.44)	40; 57
High purity	39.59 (0.13)	1.45; 1.81
Balance Ni		

* Performed using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy).

** Performed using GDMS (Glow Discharge Mass Spectrometry).

A few comments about analytical techniques used to analyze for sulfur are relevant and appropriate here.

In order to establish whether low sulfur levels indigenously present within metals and alloys were responsible for oxide scale exfoliation, a reliable analytical technique for measuring low (ppm) levels of elements of interest had to be identified. Vendor-supplied analyses are hoped to be correct but are always suspect. In addition, analyses of metals as commonly supplied by the vendor do not normally take into account non-metallic components. Furthermore, on the basis of prior experience, target alloy compositions, particularly in regard to low level additions, can be in serious error. Procedures used to produce alloys can themselves introduce low levels of impurities. Therefore, techniques had to be established that could reproducibly yield bulk sulfur analyses for concentrations of interest, i.e. less than 50 ppm by weight, in the actually prepared and homogenized alloys.

Traditionally, fusion techniques had been used to analyze bulk sulfur in metal alloys. Although widely successful in support of the ferrous metals industry, fusion techniques have yielded unsatisfactory results in the sulfur analyses of metal matrices of interest here. The problem manifested itself in poor precision of reported sulfur contents for the same specimen either analyzed at the same time or at different times. After many experimental studies, sulfur analyses based on Auger surface techniques were discounted as being unable to yield reliable or reproducible bulk sulfur contents in multiphase alloys containing significant amounts of refractory metals. The problems involving Auger analysis techniques included, but were not restricted to, such observations as preferential sulfur segregation occurring at the surface of the chromium-rich gamma phase in the two phase gamma - beta (NiAl) NiCrAl alloy (12). Thus the sulfur surface analysis of this material was highly dependent on the phase being analyzed by the Auger spectrometer; accordingly, the alloy microstructure became an important variable.

As a result of literally hundreds of analyses on many different specimens, glow discharge mass spectrometry has been found to give adequate precision to differentiate

the effects of differing low bulk alloy sulfur levels on oxide scale adherence. This precision is attested to both by the repeated random analysis of multiple MCrAl specimens from a single well homogenized ingot and by the repeated analysis of powder metallurgy-prepared materials. A large supply of these powder metallurgy specimens has been prepared from a single ingot. Because of their mode of preparation, ingot materials produced by powder metallurgy techniques should be sufficiently homogenous for this chemical analysis.

Using well homogenized alloys, chemical analysis by glow discharge mass spectrometry techniques has reproducibly indicated sulfur levels down to 1 ppm and has shown that significant differences between sulfur levels, e.g. 1-2 ppm vs. 10-20 ppm levels are readily and reproducibly distinguishable. Although both accuracy and precision are desirable in an analysis, the ability to reproducibly demonstrate differences in sulfur analyses between different materials reproducibly is paramount for these studies. The sulfur values reported here are derived from such glow discharge mass spectrometry analyses.

Yttrium additions were also made to standard purity Ni - 40 wt. % Cr alloys to characterize and compare the effect of a reactive element addition on oxidation performance. The analyzed compositions of these alloys are:

<u>Nominal Alloy Composition</u>	<u>Wt.% Cr</u>	<u>Wt.% Y</u>
Ni-40Cr-0.1Y	40.11	0.095
Ni-40Cr-0.5Y	40.63	0.55
Ni-40Cr-1.0Y	40.74	1.02
Balance Nickel		

Sulfur analyses were not performed on these alloys.

Cyclic oxidation experiments were conducted at 900°, 1000° and 1100°C. In cyclic testing, specimens were oxidized for 55 minutes at elevated temperatures then allowed to cool to ambient room temperature for five minutes before re-insertion into the high temperature zone of the furnace. Specimen weight changes would be measured after approximately every 20 cycles. Isothermal oxidation experiments were also conducted at 1000°C.

Oxidized specimens were examined by optical metallography, scanning electron microscopy using energy dispersive x-ray (EDAX) techniques and the scanning electron microprobe with wave length dispersive capabilities.

III. EXPERIMENTAL RESULTS

1. Thermogravimetric experiments.

Results of the cyclic oxidation experiments presented in Fig. 1 show that at 900°C differences between the performance of the normal purity and the high purity Ni-40Cr alloys are not marked for the approximately 1400 hours of cyclic testing.

On the other hand at 1000°C, the normal purity Ni-40Cr material shows excessive mass loss related to scale exfoliation effects, Fig. 2. In contrast, the high purity (low sulfur) Ni-40Cr alloy showed only slightly positive mass changes. Both scale exfoliation associated with the the normal purity alloy as well as scale adherence associated with the high purity Ni-40Cr alloy were confirmed by visual examination of test specimens.

To determine if scale exfoliation effects observed for the normal purity Ni - 40 wt. % Cr alloy were complicated by differences in growing oxide scales, specimens of both alloys were isothermally oxidized in air for the same time as involved in the cyclic test, i.e. 576 hours. On removal from the furnace, these test specimens (along with any spalled material) were weighed and the results are also presented in Fig. 2.

The smaller specific mass change per unit area for the high purity material as opposed to that observed for the normal purity alloy after isothermal testing suggests that a thinner oxide scale formed on the high purity alloy. (Optical metallographic observations to be presented shortly confirm this.)

At 1100°C, both the normal and high purity alloys exhibited scale exfoliation, Fig. 3. While the high purity alloy is performing better than the standard purity alloy at this temperature, the difference is essentially academic, i.e. significant scale exfoliation occurs in both cases.

Experiments were conducted to determine how yttrium additions at both usual and higher than usual concentrations affected 1000°C cyclic oxidation performance as determined by thermogravimetric experiments. Yttrium is normally added to alloys such as these at the approximately 0.1 wt. % level. Levels greater than this, i.e. 0.1 wt. %, would normally be considered unusual and would deviate from standard practice.

As seen in Fig. 4, little difference is seen between the alloys containing either no yttrium addition or yttrium added at the 0.1 wt. % level. Both alloys exhibit scale exfoliation in testing at 1000°C. Higher yttrium levels, i.e. 0.55 and 1.0 wt. % Y, seem based on thermogravimetric data alone to improve oxide scale adherence. (Optical metallographic observations which will be presented shortly do not support beneficial effects at these yttrium concentrations.)

2. Optical Metallography Studies.

In isothermal testing at 1000°C, the Ni - 40 wt. % Cr alloy made from normal quality starting materials exhibits extensive oxide exfoliation as indicated by scanning

electron microscopy techniques, Fig. 5. On the other hand for the same alloy made from high purity starting materials, adherent oxide scales are noted, Fig. 6.

Optical metallographic examination of cross sections of tested specimens support the scanning electron microscopy findings, Figs. 7 and 8 cf. Figs. 5 and 6. For the normal purity Ni - 40 wt % Cr alloy in addition to poorly adherent oxide scales as indicated in Fig. 5, extensive oxidation down grain boundaries occurs, Fig. 7. On the other hand the high purity alloy shows in addition to adherent scales, no grain boundary oxidation, Figs. 6 and 8.

Additionally it is to be specifically noted that in isothermal testing the scale formed on the high purity alloy is substantially thinner than that formed on the normal purity material, i.e. 10 microns as opposed to 20 microns, respectively, cf. Figs. 7 and 8.

Results derived from optical metallographic examination of the 1000°C cyclically tested normal and high purity specimens support observations derived from isothermal test results. Cyclically tested normal purity material indicates both preferential grain boundary oxidation as well as internal oxidation/nitridation effects, Fig. 9. On the other hand, the high purity alloy shows neither grain boundary oxidation nor internal oxidation/nitridation phenomena, Fig. 10.

Differences in oxide scale thickness between normal and high purity specimens in cyclic testing are similar to those observed after isothermal testing. Specifically the scale formed on the high purity alloy is thinner than the scale formed on the normal purity material after identical exposure, Figs. 9 and 10 cf. Figs. 7 and 8.

Recalling the thermogravimetric experiments involving additions of yttrium ostensibly added to improved oxide scale adherence, the alloys containing either zero or 0.1 wt. % yttrium additions indicated similar behavior, i.e. exfoliating scales, Fig. 4. On the other hand, specimens to which either 0.5 or 1.0 yttrium additions had been made indicated positive weight changes implying the formation of adherent protective scales, Fig. 4. Optical metallography, however, failed to confirm the formation of adherent protective scales. Rather than protective scales, exfoliating scales were observed which would indicate weight losses should have been observed in the thermogravimetric data, Fig. 4. But both extensive grain boundary and internal oxidation/nitridation effects found in these test specimens would account for the positive weight changes observed, Fig. 11.

3. Electron microprobe investigations.

Using the electron microprobe, roughly speaking similar results were observed in the case of both isothermally tested high purity and normal purity Ni - 40 wt. % Cr alloys. As was to be expected, maps for nickel and chromium indicate essentially only a chromium oxide scale, cf. Figs. 12 and 13.

Quantification of the x-ray map results by the electron microprobe indicate in the instance of both the normal and high purity alloys a chromium oxide film overlying a slightly depleted nickel - 40 wt. % chromium alloy, Figs. 14 and 15.

In the outermost layers of the oxide for both alloys, a very small nickel enrichment, amounting to a few per cent by weight, is found, Figs. 14 and 15. This nickel most likely results from transient effects occurring during the initiation of oxidation.

In the growing oxide scale, occasionally small micron sized particles enriched in nickel occur, Fig. 16. Evidence that these particles are elemental nickel is based both on x-ray maps which indicate the presence of nickel and the absence of chromium and oxygen and on deliberate point mode analyses with the microprobe confirming the x-ray map results just mentioned, Fig. 17.

Of prime importance with regard to oxide scale adherence effects, x-ray maps using the electron microprobe failed to reveal any evidence for sulfur at the scale-metal interface for either the normal or high purity alloys.

However using the microprobe in its most sensitive mode, i.e. slow line scans, qualitative information about impurities at trace levels can frequently be obtained. Using the microprobe in this mode, sulfur has been observed at the scale-metal interface in the case of the normal purity alloy. This information is presented both by a line scan pictorially superimposed over the particular area of the specimen examined and by a traditional graph of composition (in relative terms) vs. distance, Figs. 17 and 18.

Despite repeated attempts, similar studies involving the high purity Ni - 40 wt. % Cr alloy failed to produce a signal above background signal levels which could be associated with a sulfur enrichment at the scale-metal interface.

IV. DISCUSSION

Prior work conducted at UTRC which has subsequently and increasingly been supported by investigators elsewhere have shown the importance of indigenous sulfur present at levels previously considered to be innocuous having substantial effects on oxide scale adherence (7, 8, 10, 11, 12, 13, 14). With the exception of cursory work by Lees, the vast majority of those studies dwell with alumina formers (14).

In work reported here, studies were conducted to determine if factors--specifically, sulfur segregation--affecting oxide adherence in alumina formers were also applicable in the case of chromia formers. While similarity in behavior would have been nice to have postulated in the case of these two scales, there is no *a priori* reason to believe factors affecting the adherence of one of these scales would also be important in the adherence of the other. After all, alumina and chromia are chemically different.

Amplifying slightly on the concern about generalizing from the behavior of alumina scales with regard to sulfur segregation effects, studies were conducted with elemental nickel to determine if sulfur segregation affected oxide scale adherence there. In those studies, no effect of sulfur on oxide scale adherence was noted (16). It is to be kept in mind that nickel oxidation is thought to largely depend upon outward diffusion of nickel to the scale-gas interface (17). For alumina formation, oxidation is largely controlled by inward diffusion of oxygen down grain boundaries regardless of whether or not a reactive element such as yttrium is present (1). On the other hand for chromia formation in the absence of a reactive element, such as yttrium, inward grain boundary diffusion of oxygen predominates whereas with yttrium additions outward diffusion of chromium is controlling (18-23).

Hence these studies were conducted to pursue the question about whether sulfur segregation effects were also important in the adherence of protective chromia scales.

In the fabrication of the Ni - 40 wt. % Cr alloy, distinct differences have been observed with regard to sulfur content depending upon the purity of the starting material. The Ni - 40 wt. % Cr alloy made from normal purity metals has been found to contain approximately 40 to 60 ppm by weight sulfur. For the alloy made from high purity metals, the sulfur content is in the range of 1 to 2 ppm by wt. (It is to be noted and re-emphasized that the analyses and results of studies reported here are based on well homogenized alloys.)

These results are in precise and exact agreement with prior studies involving alumina formers. Based upon literally hundreds of analyses involving a wide range of specimens, employing blind specimens and repetitive tests conducted at widely spaced time intervals, the glow discharge technique has reliably been able to distinguish and differentiate materials with sulfur contents in the approximately 1 to 50 ppm by weight concentration (24).

In cyclic testing at 900°C, the sulfur content of the starting alloy little affected alloy performance with regard to oxide scale adherence, i.e. scales formed are quite adherent on both materials, Fig. 1. At 1100°C, again both alloys are performing similarly, i.e. scale exfoliation effects predominate, Fig. 3. The poor performance shown by chromia formers at 1100°C is not unexpected. Chromia formers traditionally perform poorly at such high temperatures, (e.g., 25). For applications requiring exposure to temperatures such as 1100°C, alumina scale-forming alloys are traditionally selected over materials which develop protective chromia scales.

However in 1000°C testing, the sulfur content of the nickel chromium alloy markedly affects oxide scale adherence, Fig. 2. Here the normal purity alloy continually exfoliates scales in thermal cycling while adherent scales have formed on the high purity material for the 576 hour testing reported here.

Furthermore in support of the cyclic experiments and based upon weight change behavior data, isothermal testing conducted indicates less oxidation of the high purity alloy than for the normal purity alloy. Differences in mass change convert directly to differences in oxide scale thickness, i.e. thinner scales form on the high purity alloy. This assertion is based upon both the mass change data presented for the isothermal test as well as the metallographic cross sections of relevant specimens, e.g. Figs. 4, 7 and 8. Ten and twenty micron thick scales formed on the high and normal purity Ni - 40 wt. % Cr alloys, respectively, after 576 hours exposure.

Hence not only do high purity Ni - 40 wt. % Cr alloys form more adherent scales than those formed on the normal purity material but they also form scales which while more protective are thinner. Thinner protective scales would be preferred because stresses directly related to oxide scale thicknesses would be minimized.

In the cases of both normal purity alumina and chromia forming alloys, sulfur enrichments occur at the scale-metal interface, Fig. 18 and Fig. 8 in Ref. 8. These sulfur enrichments are not detected by the electron microprobe in similar investigations involving high purity, i.e. low sulfur, alloys.

Interestingly the addition of yttrium at the 0.1 wt. % level does not improve the performance of the alloy based upon its resistance to oxide scale exfoliation, Fig. 4. This result differs from that commonly observed in the case of alumina-forming alloys, e.g. Ref. 8. Furthermore increased yttrium additions (0.5 wt. % and greater) seem to improve oxide scale adherence based on the thermogravimetric data alone, Fig. 4. However when these specimens are metallographically polished, the improvement is quickly seen to be illusory. Poor oxide adherence which would be associated with weight loss effects is counterbalanced by internal oxidation/nitridation effects which yield slight positive weight gains, Figs. 4 and 11.

Hence in 1000°C testing, the yttrium addition does not improve performance. The intrinsic sulfur content of the alloy (without the necessity of an yttrium addition) strongly effects both oxide scale adherenced and growth kinetics for the test conditions investigated here. The finding that the purity of the Ni - 40 wt. % Cr alloy affects oxide growth kinetics has not been previously reported.

V. SUMMARY AND CONCLUDING REMARKS

- Sulfur is a common indigenous impurity in nickel-based alloys.
- Glow discharge mass spectrometry (GDMS) techniques have been found to reliably and reproducibly differentiate sulfur contents in the low ppm (by weight) range.

- Ni-40 wt. % Cr made from standard and high purity starting metals and homogenized were found to contain approximately 40-60 and 1-2 ppm sulfur, respectively.
- In cyclic testing at 900°C and 1000°C, similar results were shown by both alloys. At 900°C, adherent scales were formed while at 1100°C both alloys exfoliated scales. Although the high purity alloy showed less scale exfoliation, because scale exfoliation did occur the differences are essentially academic.
- At 1000°C, the normal purity alloy exhibited exfoliation while the high purity alloy showed no exfoliation for 576 hours of cyclic testing.
- Isothermal tests indicated that the higher purity alloy formed a thinner scale (10 microns) than that which formed on the normal purity alloy (20 microns) in 576 hours of 1000°C exposure. Hence these studies indicate that the isothermal oxidation kinetics of alloys such as Ni-40 wt. % Cr depend upon the sulfur content of the base alloy.
- At the scale-metal interface for the normal purity alloy, a sulfur enrichment could be discerned by the electron microprobe. For the high purity alloy similarly examined, no such sulfur enrichment could be discerned. This result replicates what had similarly been observed and previously reported in the case of oxidized normal and high purity NiCrAl alloy specimens (8).
- Contrary to studies involving alumina formers, yttrium additions to the level of 0.5 wt. % did not improve scale adherence. While additions to the level of 1 wt. % gave the illusion of improving oxidation resistance based on mass change behavior, optical metallographic examination of tested specimen revealed both scale exfoliation and internal oxidation/nitridation. The latter phenomena would account for the slightly positive mass changes observed in cyclic oxidation experiments.

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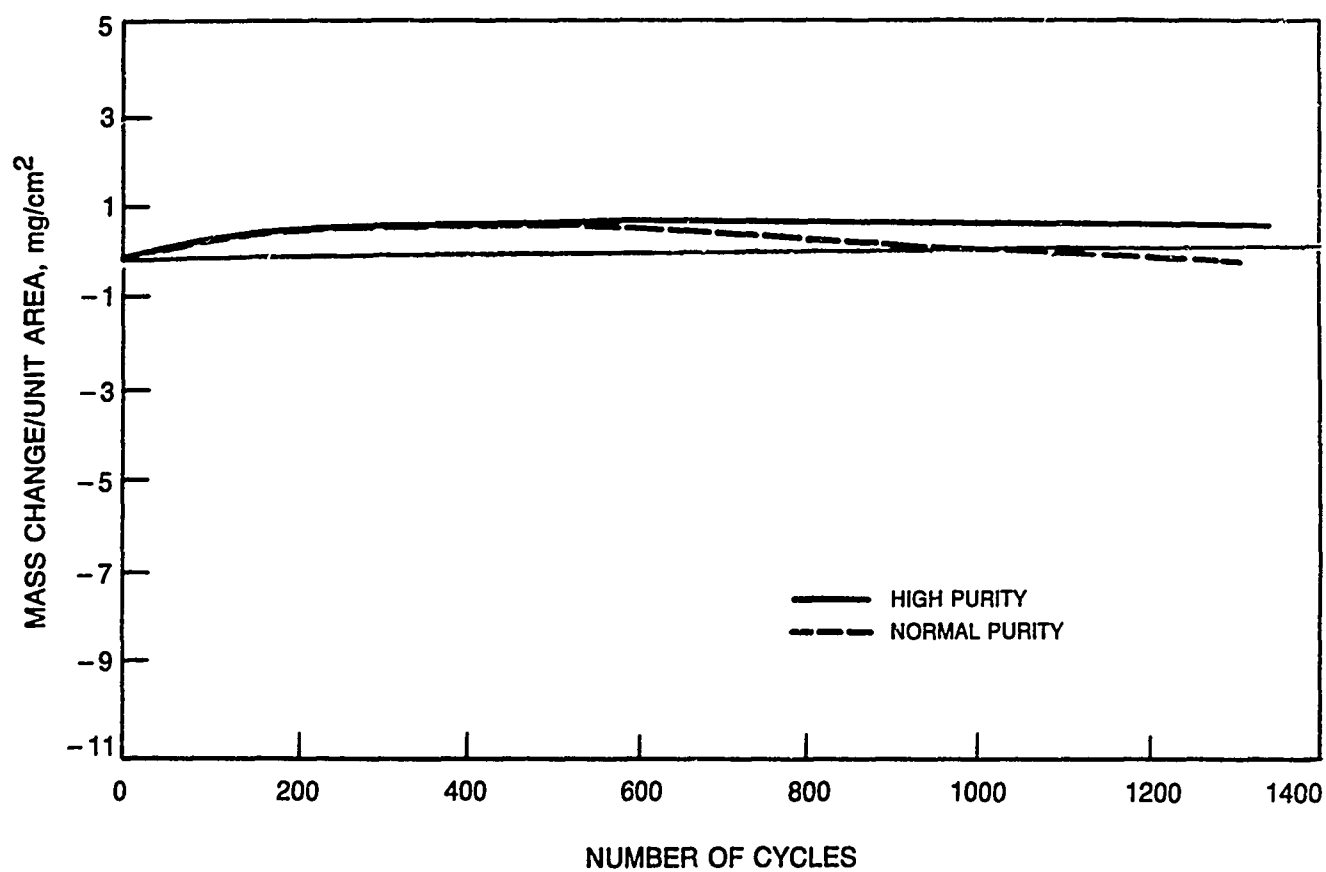


Fig. 1. A Comparison of the 900°C Cyclic Oxidation Behavior of Normal Purity and High Purity, i.e. Normal Sulfur and Low Sulfur, Ni-40 wt. % Cr Alloys

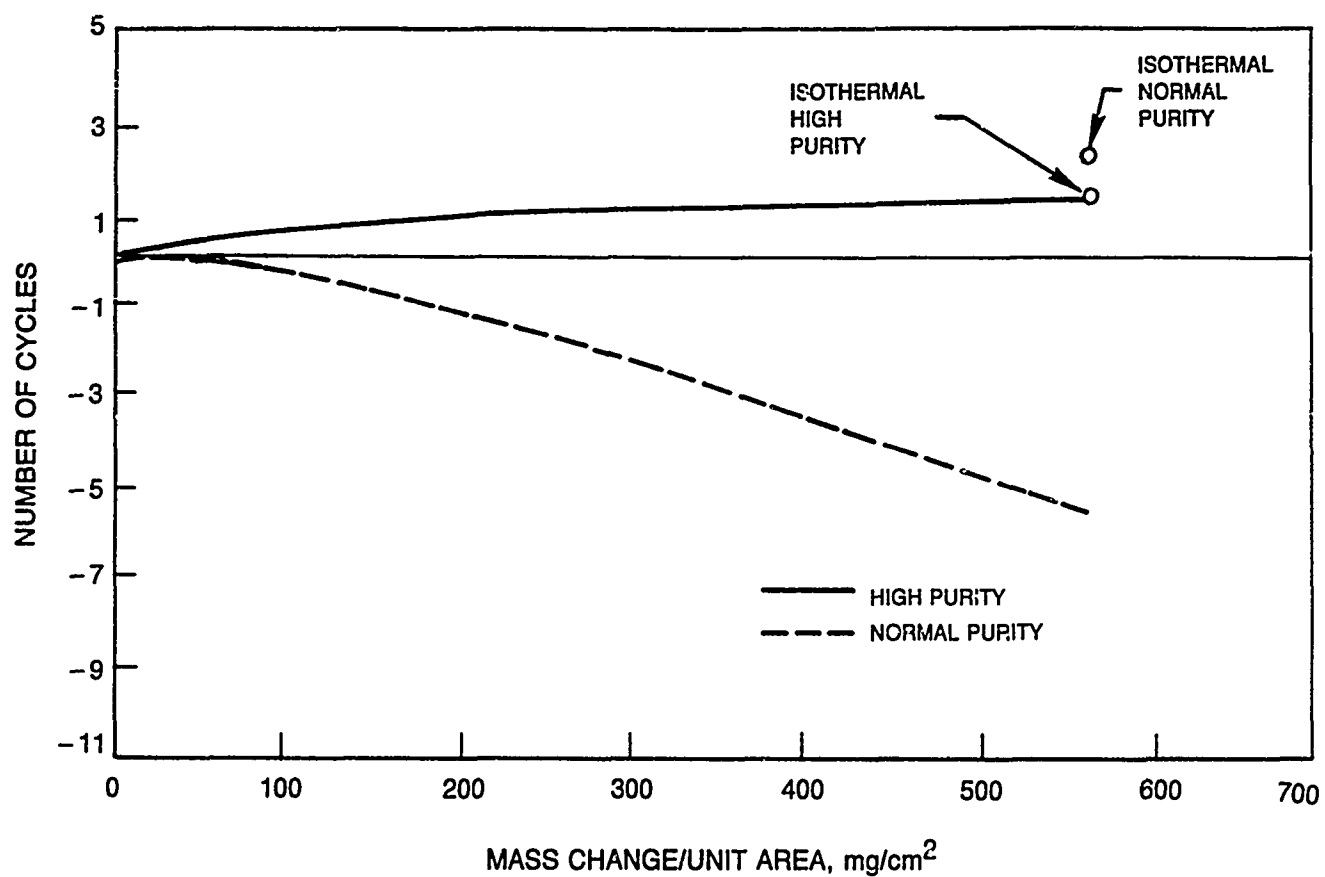


Fig. 2. A Comparison of the 1000°C Cyclic Oxidation Behavior of Normal Purity and High Purity, i.e. Normal Sulfur and Low Sulfur, Ni-40 wt. % Cr Alloys

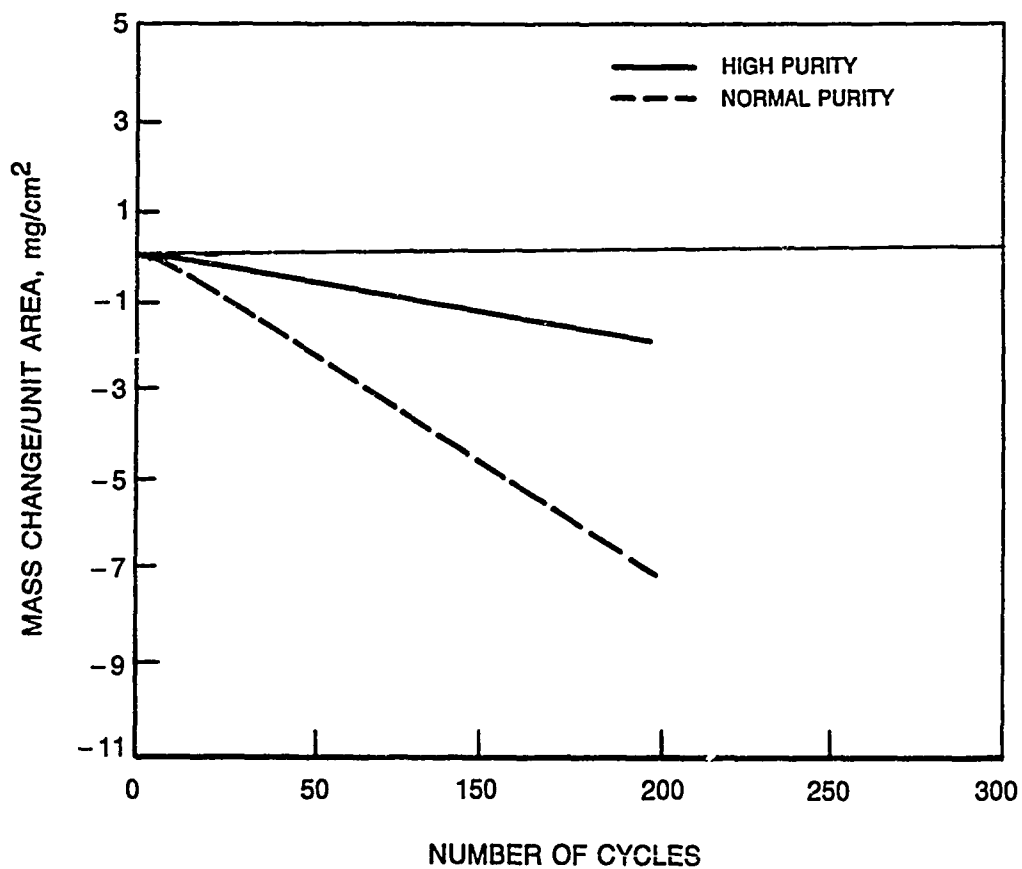


Fig. 3. A Comparison of the 1100°C Cyclic Oxidation Behavior of Normal Purity and High Purity, i.e. Normal Sulfur and Low Sulfur, Ni-40 wt. % Cr Alloys

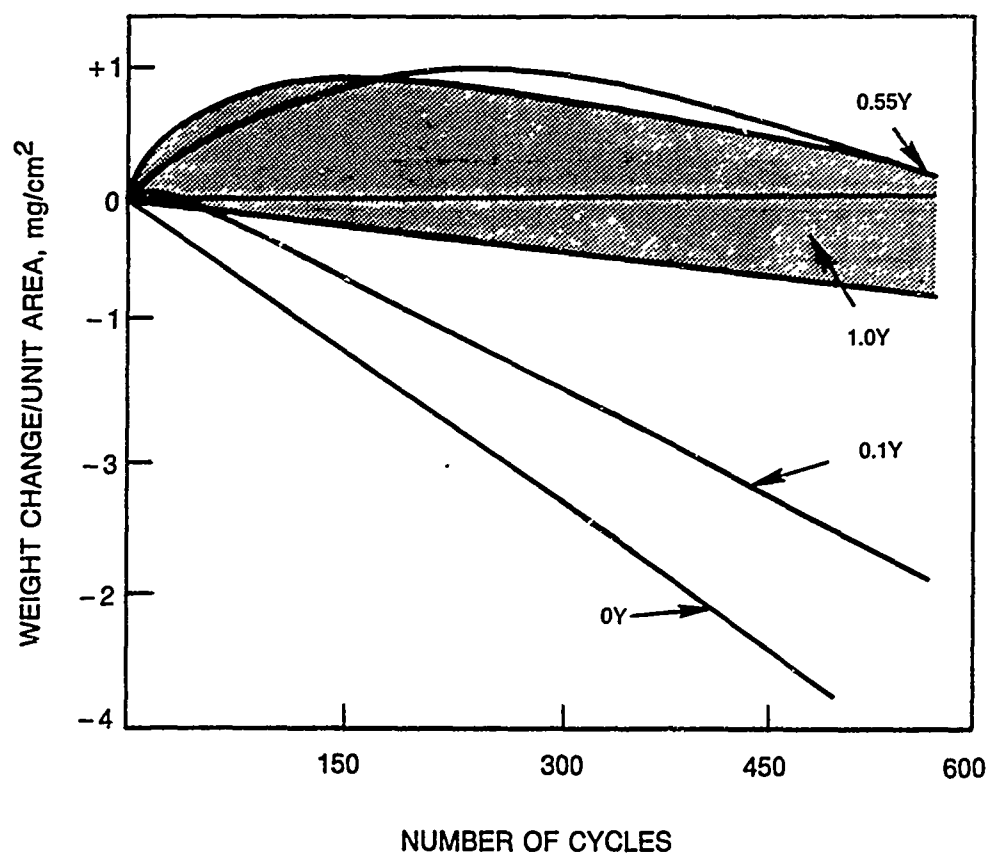


Fig. 4. The Effect of Yttrium Additions on the 1000°C Oxidation Behavior of Normal Purity Ni-40 wt. % Cr Alloys

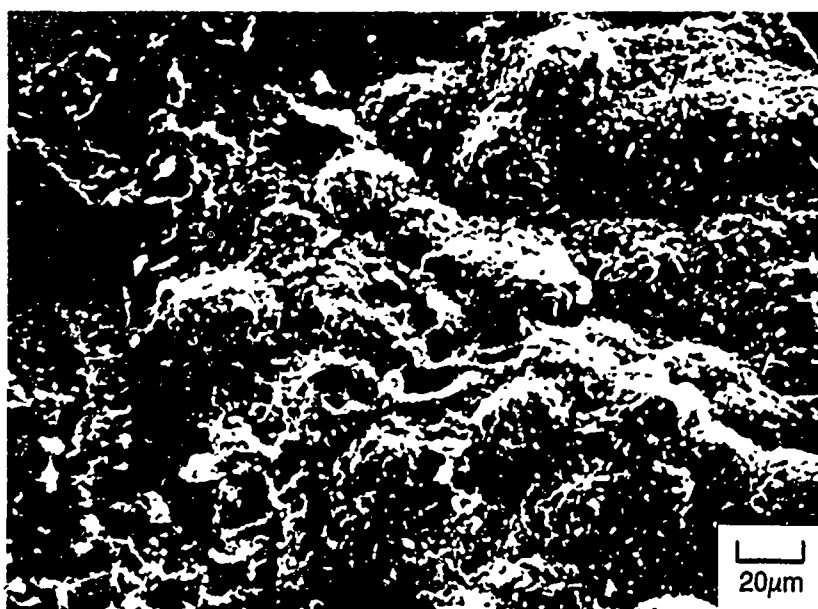
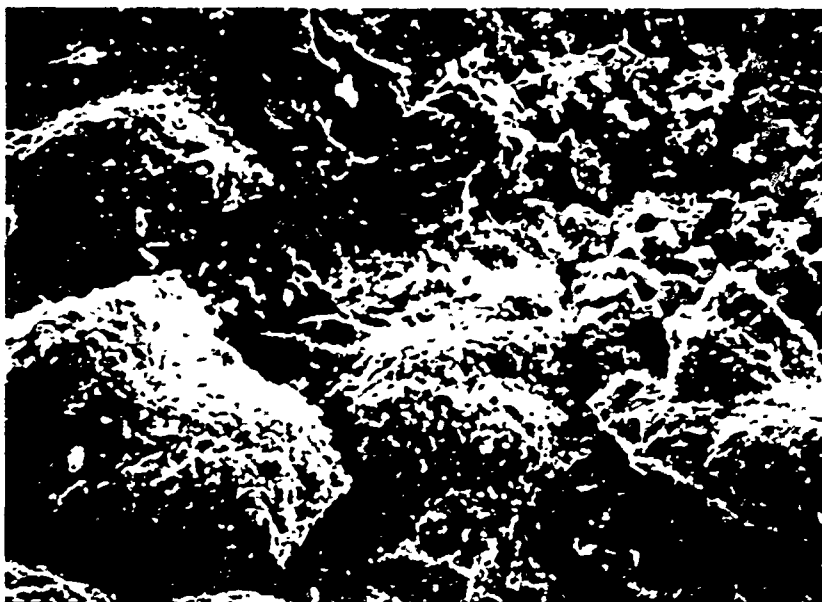


Fig. 5. Exfoliating Oxide Scales Formed on Normal Purity Ni-40 wt. % Cr After 576 hours of Isothermal Oxidation at 1000°C. Scanning Electron Microscopy.

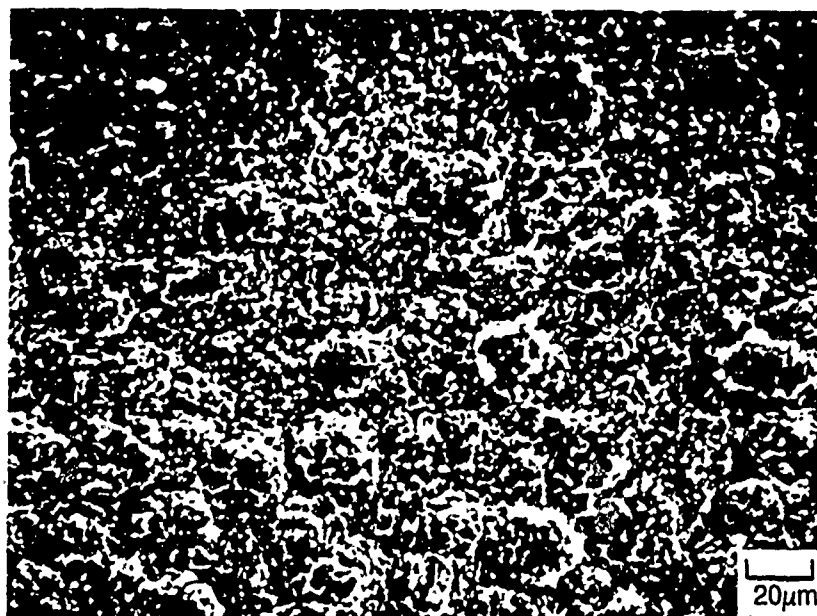
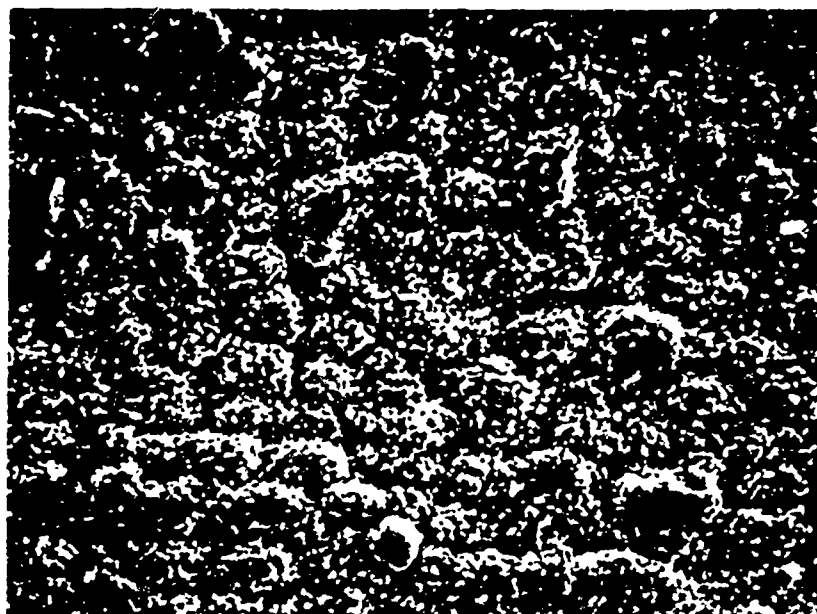


Fig. 6. Adherent Oxide Scales Formed on High Purity Ni-40 wt. % Cr After 576 hours of Isothermal Oxidation at 1000°C. Scanning Electron Microscopy.

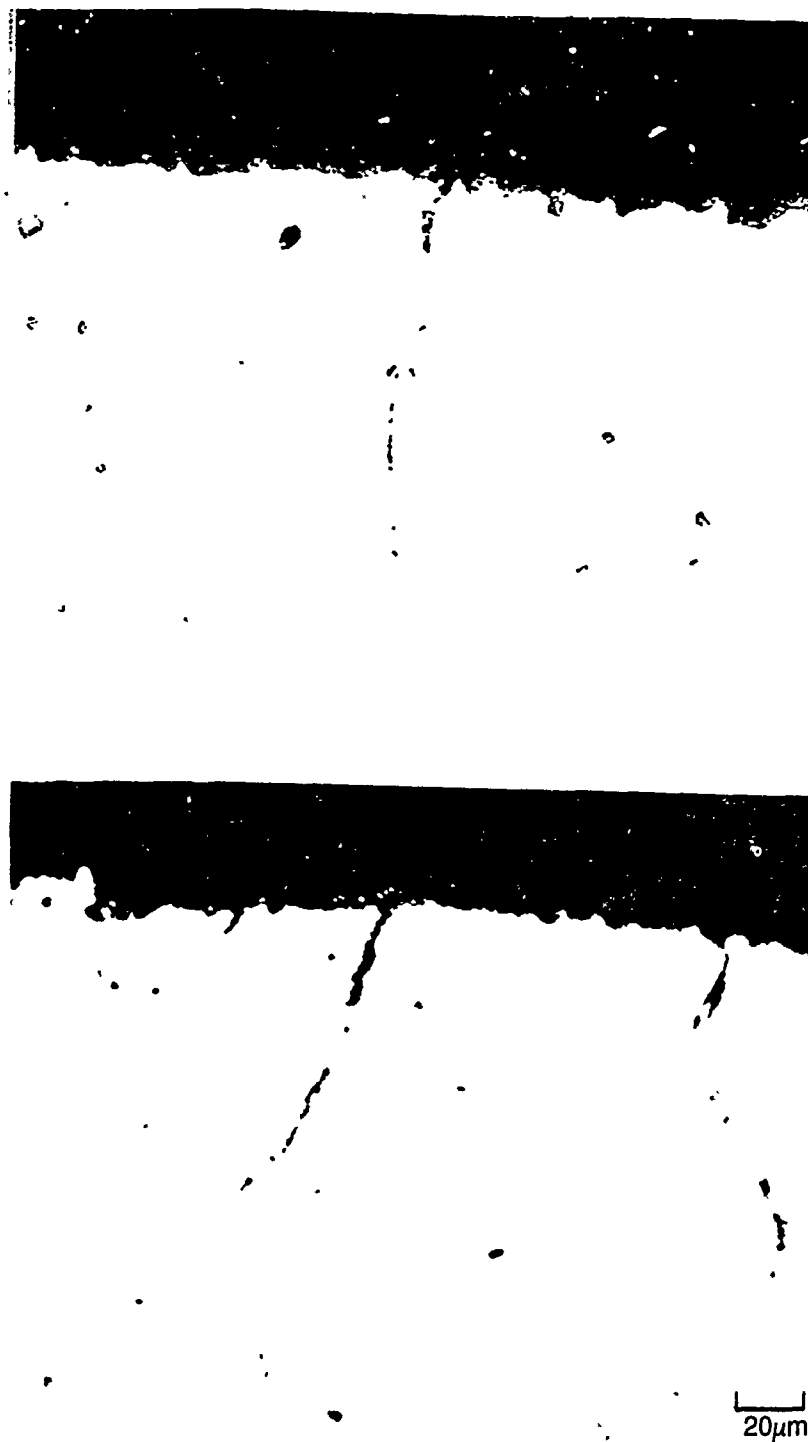


Fig. 7. Cross Section of Normal Purity Ni-40 wt. % Cr Alloy Formed After 576 hours of Isothermal Oxidation at 1000°C. Optical Metallography.



20 μ m

Fig. 8. Optical Section of High Purity Ni-40 wt. % Cr Alloy After 576 hours of Isothermal Oxidation at 1000°C. Optical Metallography.

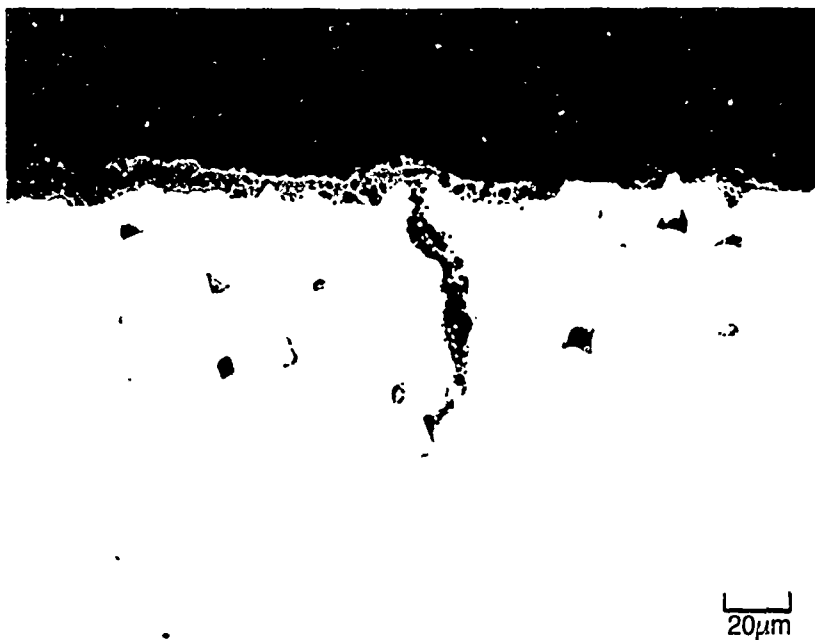


Fig. 9. Cross Section of Normal Purity Ni-40 wt. % Cr Alloy After 576 hours of Cyclic Testing to 1000°C. Optical Metallography.



20 μ m

**Fig. 10. Cross Section of High Purity Ni-40 wt. % Cr Alloy
After 576 hours of Cyclic Testing to 1000°C.
Optical Metallography.**

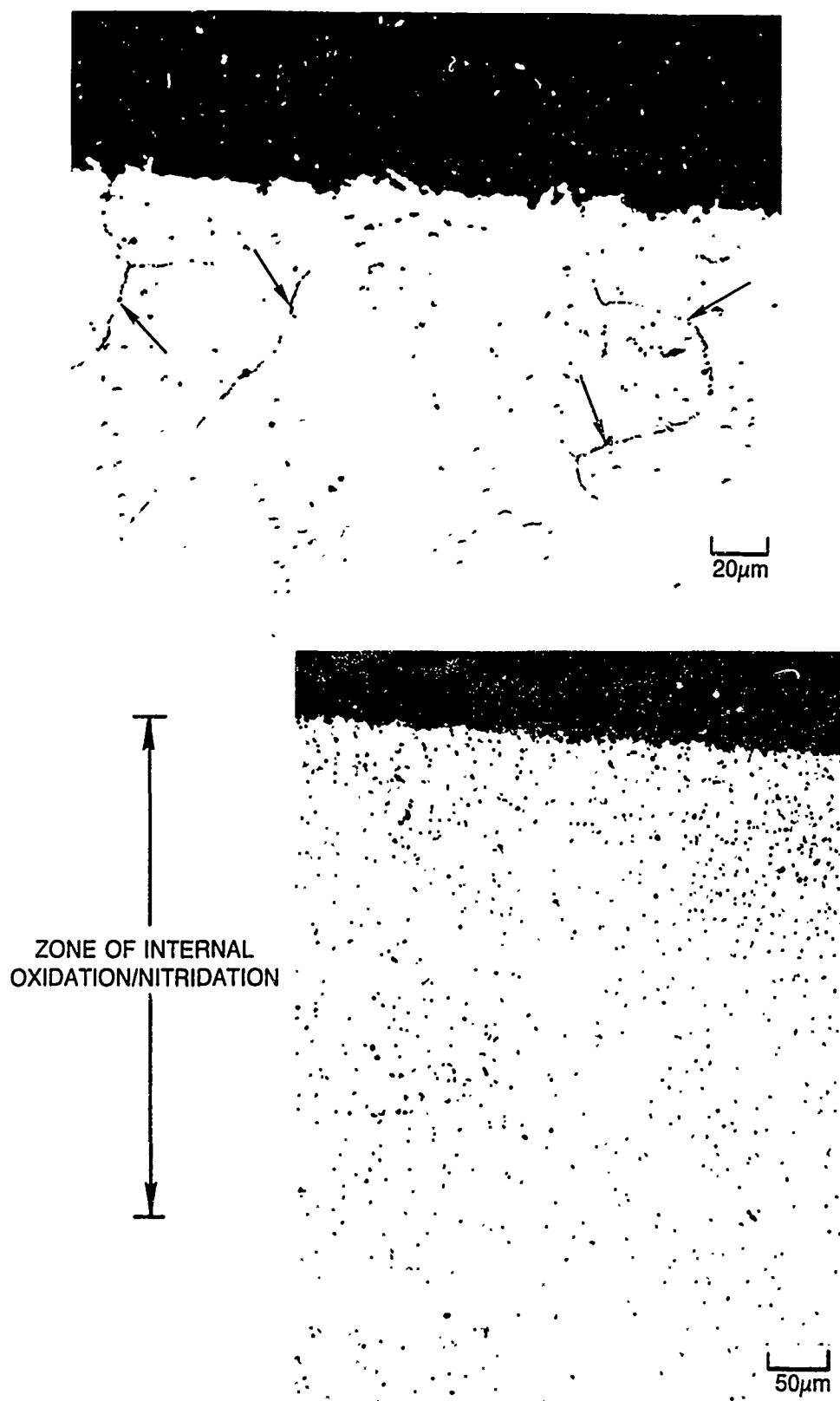


Fig. 11. Cross Section of Normal Purity Ni-40 wt. % Cr-1 wt. % Y Alloy After 562 Cycles of Testing to 1000°C Showing Both Grain Boundary and Internal Oxidation/Nitridation Effects. [Similar Results Were Observed for the Ni-40 wt. % Cr-0.5 wt. % Y Alloy, cf. Fig. 4] Optical Metallography. Arrows Indicate Grain Boundary Oxidation Effects.

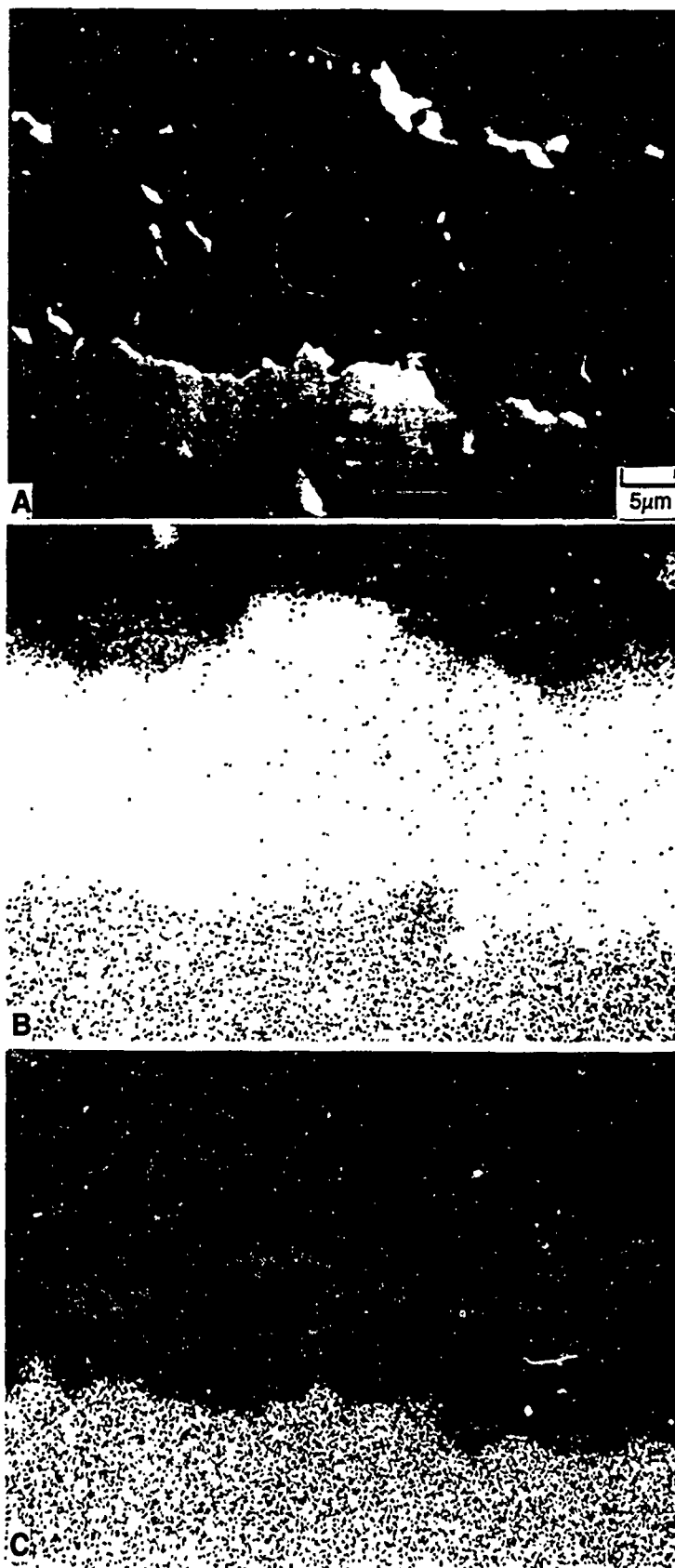


Fig. 12. X-ray Maps for Normal Purity Ni-40 wt. % Cr Oxidized Isothermally for 576 hours at 1000°C in Air. Electron Microprobe Studies.
A. Back Scattered Electron Micrograph
B. X-ray Map for Chromium
C. X-ray Map for Nickel

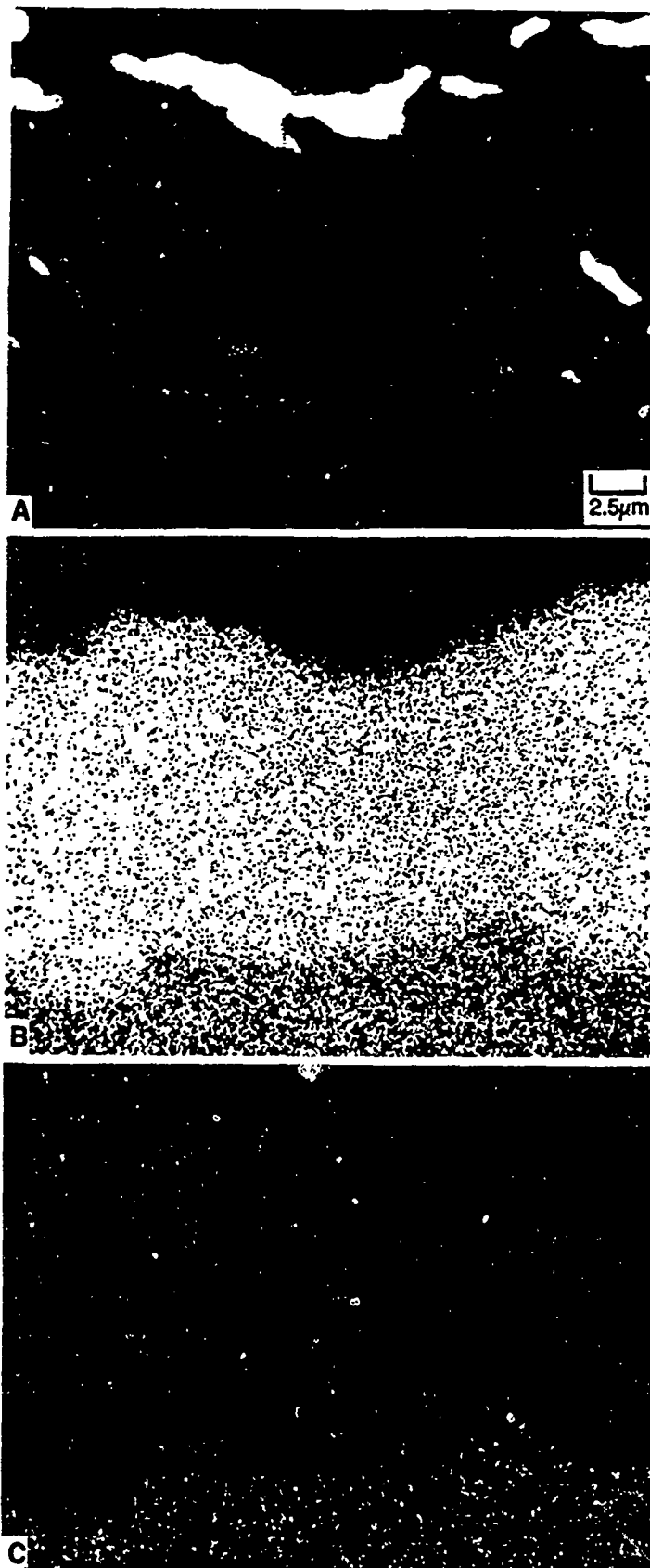


Fig. 13. X-ray Maps for Normal Purity Ni-40 wt. % Cr Oxidized Isothermally for 576 hours at 1000°C in Air. Electron Microprobe Studies.
A. Back Scattered Electron Micrograph
B. X-ray Map for Chromium
C. X-ray Map for Nickel

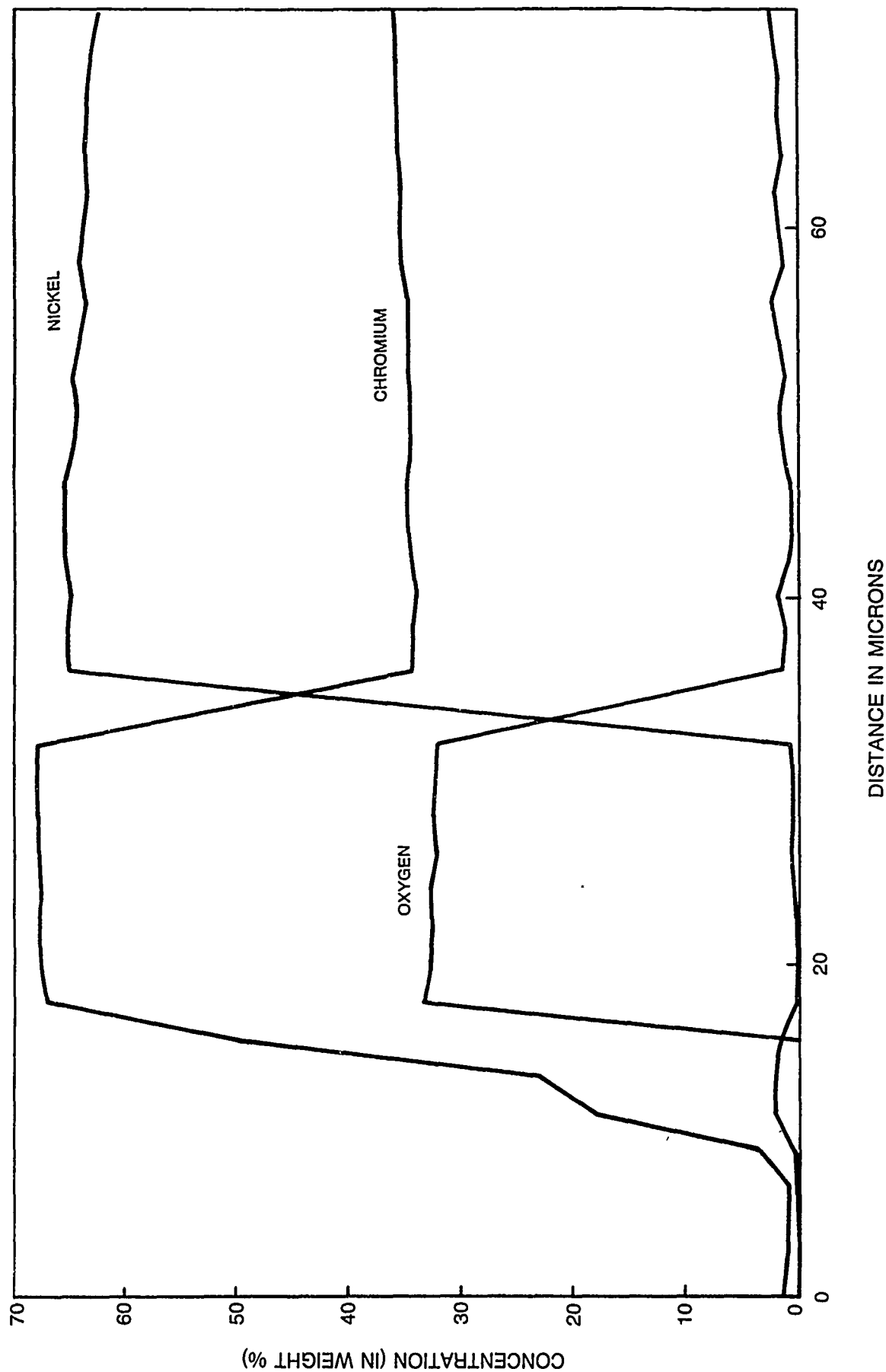


Fig. 14. Bulk Composition Across the Oxide Scale Formed on Normal Purity Ni-40 wt. % Cr Isothermally Oxidized in Air at 1000°C for 576 hrs. Electron Microprobe Results.

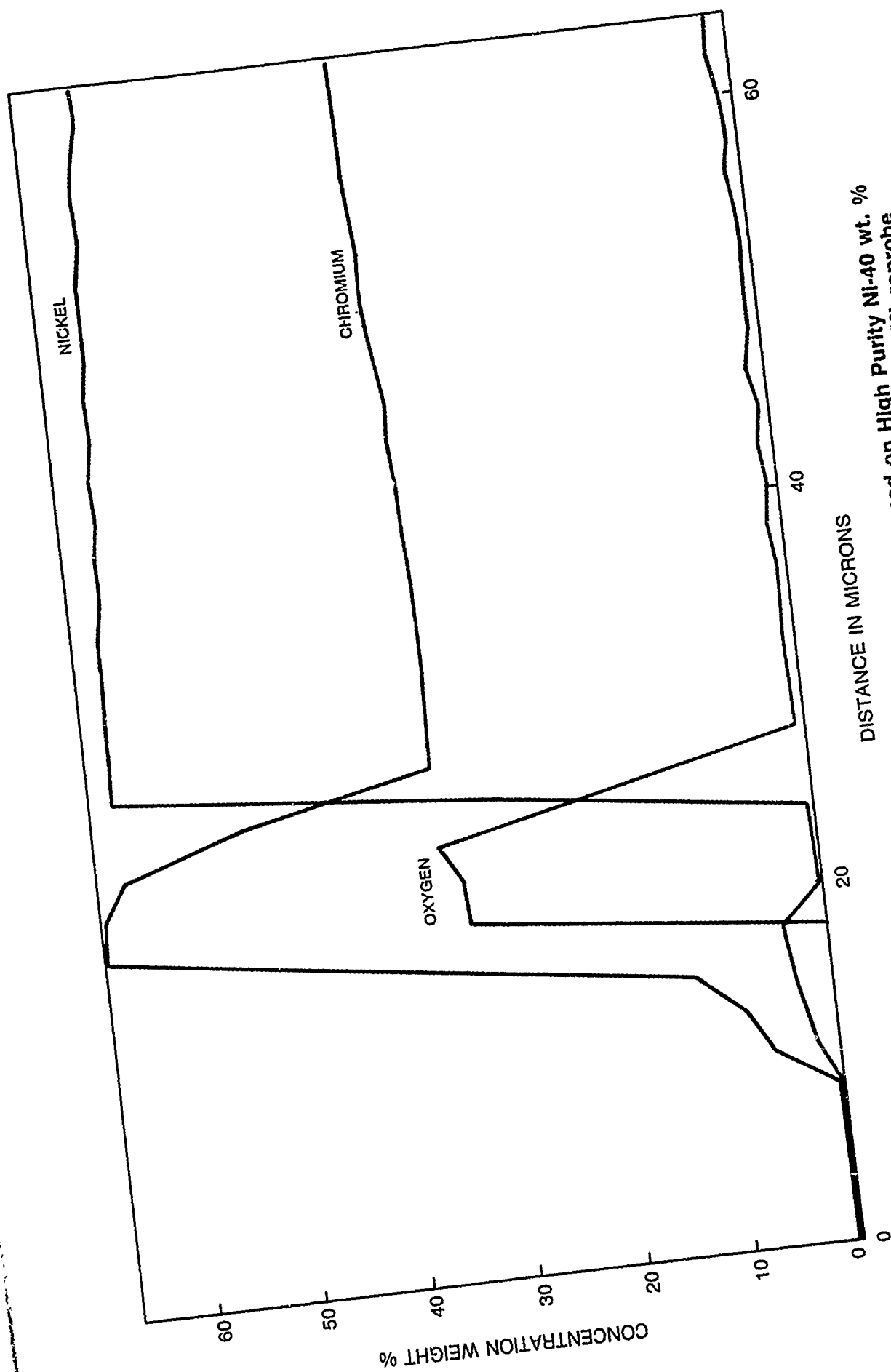


Fig. 15. Bulk Composition Across the Oxide Scale Formed on High Purity Ni-40 wt. % Cr Isothermally Oxidized in Air at 1000°C for 576 hrs. Electron Microprobe Results.

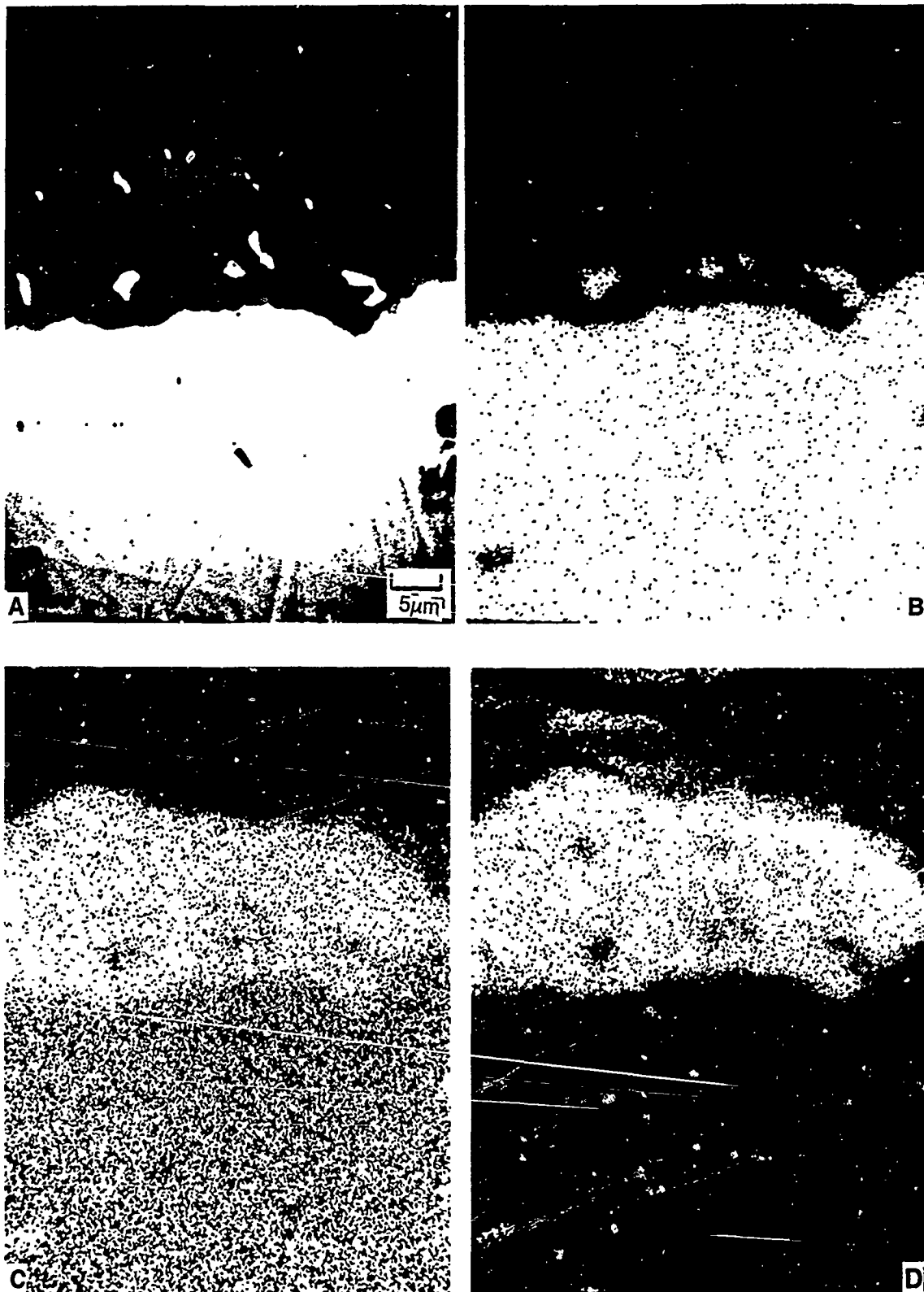


Fig. 16. Elemental Nickel Particles Entrapped Within the Growing Chromium Oxide Scale, cf. Fig. 14. Electron Microprobe Studies.

- A. Backscattered Electron Micrograph**
- B. X-ray Map for Nickel**
- C. X-ray Map for Chromium**
- D. X-ray Map for Oxygen**

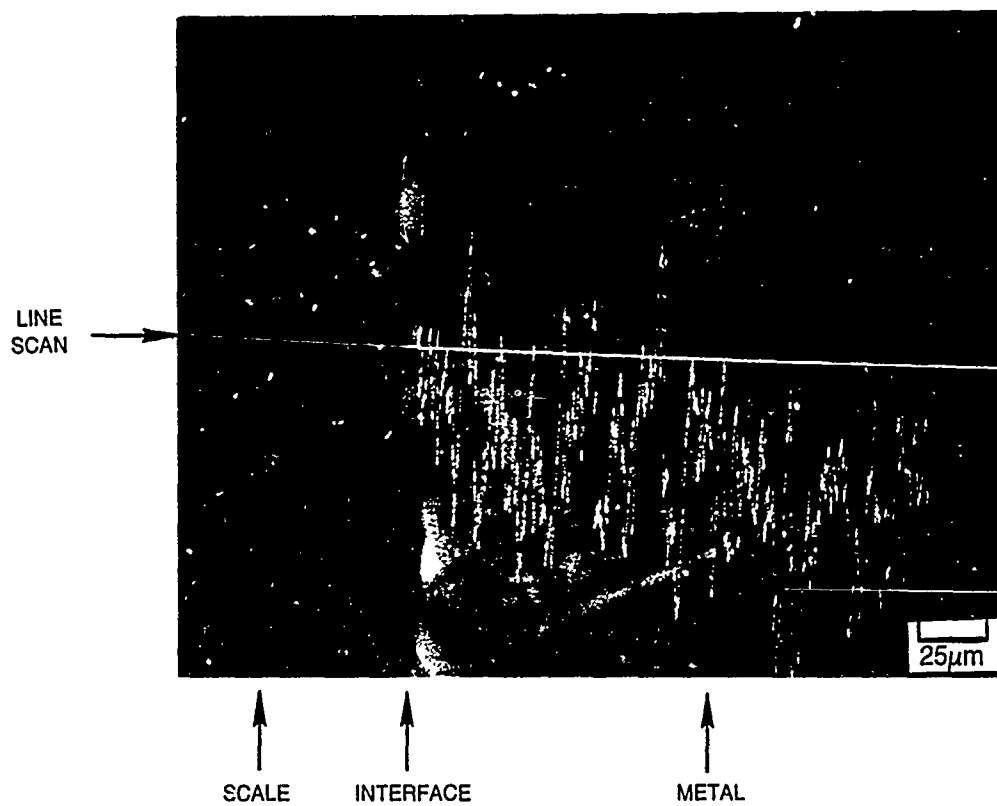


Fig. 17. Sulfur Detected at the Scale-Metal Interface for Normal Purity Ni-40 wt. % Cr, cf. Fig. 14. Electron Microprobe Results. Line Scan Superimposed on Back Scattered Electron Micrograph

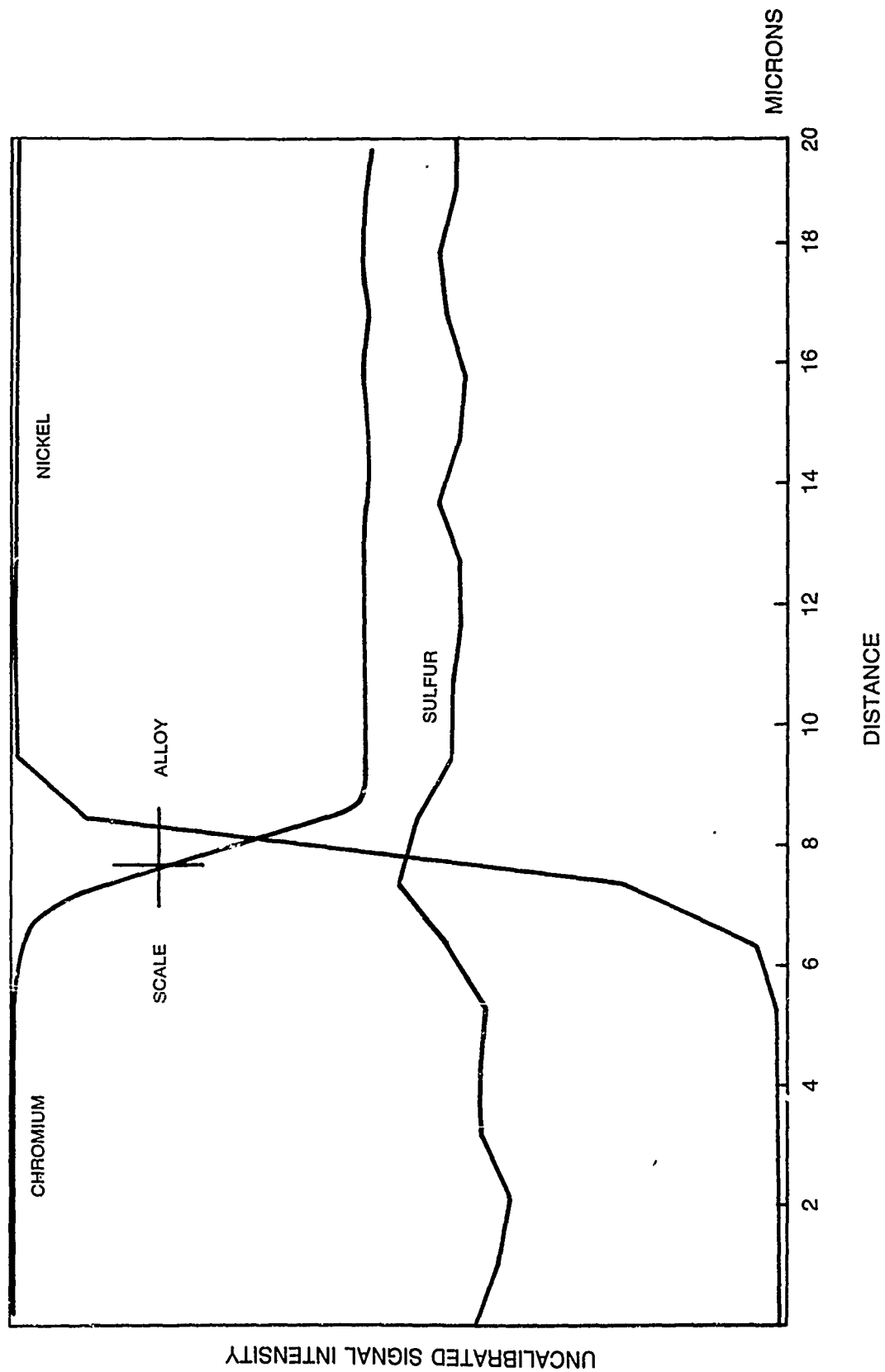


Fig. 18. Sulfur Detected at the Scale-Metal Interface for Normal Purity Ni-40 wt. % Cr, cf. Fig. 14. Electron Microprobe Results. Data Presented in Terms of Uncalibrated Signal Intensity vs Distance.

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